



DECLARATION

I, Noriko SHINTANI, Patent Attorney, of SIKs & Co., 8th Floor, Kyobashi-Nisshoku Bldg., 8-7, Kyobashi 1-chome, Chuo-ku, Tokyo 104-0031 JAPAN hereby declare that I am the translator of the certified official copy of the documents in respect of an application for a patent filed in Japan on March 29, 2002 under Patent Application No. 093943/2002 and that the following is a true and correct translation to the best of my knowledge and belief.

Dated: September 27, 2005

Noriko Shintani
Noriko SHINTANI



PATENT OFFICE

JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy of the following application as filed with this office.

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Applicant(s) : Mitsubishi Chemical Corporation

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[Title of the Invention] Hair Cosmetic Polymer Composition and Hair Cosmetic Using the Same
[Number of Claims] 8
[Inventor]
[Domicile or Residence] c/o Mitsubishi Chemical Corporation,
1, Toho-cho, Yokkaichi-shi, Mie
[Name] Minako SHIBATA
[Inventor]
[Domicile or Residence] c/o Mitsubishi Chemical Corporation,
1, Toho-cho, Yokkaichi-shi, Mie
[Name] Tomoaki HIWATASHI
[Applicant for Patent]
[Identification Number] 000005968
[Name] Mitsubishi Chemical Corporation
[Administrator]
[Identification Number] 100095843
[Patent Attorney]
[Name] Junji KAMATA
[Telephone Number] 03-3538-5680
[Administrator]
[Identification Number] 100092635
[Patent Attorney]
[Name] Hisao SHIOZAWA
[Administrator]
[Identification Number] 100096219
[Patent Attorney]
[Name] Masazumi IMAMURA
[Fee]
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English translation of Japanese Patent Application No. 2002-093943 (filed Mar. 29, 2002)

[Name of document] Specification

[Title of the invention] HAIR COSMETIC POLYMER COMPOSITION AND HAIR COSMETIC USING THE SAME

[Claims]

[Claim 1] A hair cosmetic polymer composition comprising (a) a block copolymer having a number-average molecular weight of 1.0×10^3 to 1.0×10^6 , and having two or more glass transition points or melting points and (b) an anionic polymer (b) in a ratio by weight ((a)/(b)) of 1/10 to 10/1.

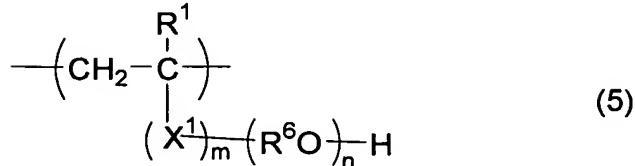
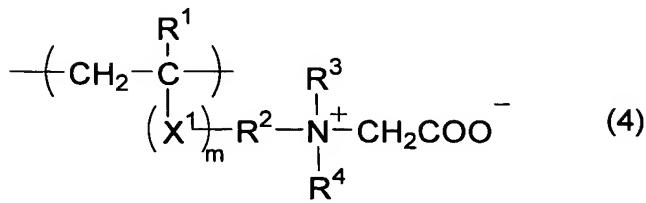
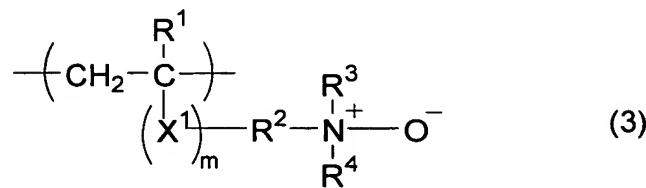
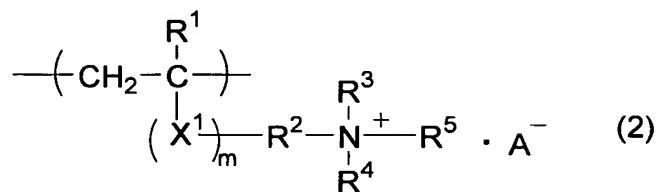
[Claim 2] The hair cosmetic polymer composition as set forth in claim 1, wherein the block copolymer (a) comprises at least one block formed of a unit having at least one hydrophilic group selected from groups consisting of an anionic group consisting of carboxylic acid group, sulfonic acid group, phosphonic acid group and salts of these groups; a cationic group consisting of amino group (including quaternary ammonium salt group), pyridyl group and salts of these groups; a nonionic group consisting of hydroxyl group, alkoxy group, epoxy group, amido group and cyano group; an amphoteric ionic group consisting of carboxybetaine group; and a semipolar group consisting of amine oxide group.

[Claim 3] The hair cosmetic polymer composition as set forth in claim 1 or 2, wherein the anionic polymer (b) is a polymer having an anionic group selected from carboxyl group, sulfonic acid group, phosphonic acid group and salts of these groups.

[Claim 4] The hair cosmetic polymer composition as set forth

in any one of claims 1 to 3, wherein the block copolymer (a) comprises at least one of units represented by formulae (1) to (5) below:

[Chemical structure 1]



(where, R^1 represents a hydrogen atom or a methyl group; R^2 and R^6 respectively represent a C_{1-4} straight-chain or branched-chain alkylene group; R^3 , R^4 and R^5 respectively represent a hydrogen atom, C_{1-24} alkyl group, C_{6-24} aryl group, or any combination thereof such as C_{7-24} arylalkyl group or alkylaryl group; and X^1 represents $-\text{COO}-$, $-\text{CONH}-$, $-$

O- or NH-. A⁻ represents an anion; and M represents a hydrogen atom, an alkali metal ion or an ammonium ion. m is 0 or 1; and n is any integer from 1 to 50.)

[Claim 5] The hair cosmetic polymer composition as set forth in any one of claims 1 to 4, wherein the block copolymer (a) is a di-block copolymer, tri-block copolymer or multi-block copolymer.

[Claim 6] The hair cosmetic polymer composition as set forth in any one of claims 1 to 5, wherein the block copolymer (a) comprises a unit derived from an ethylenic unsaturated carboxylic acid in an amount of 10 to 90% by weight, and a unit derived from an ethylenic unsaturated carboxylate ester in an amount of 90 to 10% by weight.

[Claim 7] A hair cosmetic comprising a hair cosmetic polymer composition as set forth in any one of claims 1 to 6 in an amount of 0.1 to 10% by weight.

[Claim 8] The hair cosmetic as set forth in claim 7 further comprising gas or liquid for spray.

[Detailed description of the invention]

[0001]

[Technical field of the invention]

The present invention relates to hair cosmetic polymer compositions prepared by combining a block copolymer and an anionic polymer, and hair cosmetics using the same. The compositions of the present invention are excellent in hair styling performance and in hair styling keep performance, and capable of giving good feeling finish; and, thus, they are useful for hair sprays, hair muses, hair set lotions, hair gels or the like.

[0002]

[Related art]

As hair styling products, solutions prepared by dissolving polymers, capable of film-forming, in water, lower alcohol or mixture thereof, have been used. Such hair styling products are applied to hairs and dried, and then can give styling performance of keeping hairs in a desired style. As polymers capable of film-forming, anionic polymers have been used widely. In order to improve hair styling performance, anionic polymers which form a stiff and not flexibel film have been used, and hair styling products using such polymers suffer from a problem of stiff feeling under a dried condition and cannot give sufficient styling performance. Hairs done with such hair styling products suffer from flaking phenomenon when they are combed, and are untidy and unruly hairs due to electrostatic charge and, thus, such hair styling products are not sufficient.

[0003]

In order to solve such problems, especially in order to improve soft feeling, cosmetic additives such as oils or surfactants have been added to anionic polymers. Addition of such additives, however, lowers hair styling performance, and hair styling products balanced in performances have never been obtained. In Japanese Laid-Open Patent Publication No. syo 55-59107, a hair cosmetic composition prepared by combining an anionic polymer and a cationic polymer is proposed; and, on the other hand, in Japanese Laid-Open Patent Publication No. syo 56-92813, a hair cosmetic composition prepared by combining an anionic

polymer and an amphoteric ionic polymer is proposed. And, Japanese Laid-Open Patent Publication No. hei 10-87439, a hair cosmetic composition prepared by combining an anionic polymer and an amine oxide containing polymer is proposed as a hair styling product excellent in flexibility and hair styling performance.

[0004]

[Problems to be solved by the invention]

However, hair styling products employing these combinations are not sufficient from view of performances such as style recovery performance, hair style performance, or finishing performance.

The present invention is provided in order to solve the above mentioned problems, and one object of the present invention is to solve problems of the conventional hair cosmetic polymer composition using anionic polymers, and to provide a hair cosmetic polymer composition and a hair cosmetic material having an excellent hair-styling ability and an excellent hair-style-keeping ability and giving natural-feeling finishing without unpleasant feeling.

[0005]

[Means of solving the problems]

Under the above circumstances, in order to solve the above mentioned problems, the present inventors conducted various studies, and as a result, they found that a hair cosmetic polymer composition, having an excellent hair-styling ability and an excellent hair-style-keeping ability and giving natural-feeling finishing without unpleasant feeling, can be obtained by combining an anionic polymer and

a certain block copolymer. On the basis of the finding, the present invention was achieved.

[0006]

In order to solve the above mentioned problems, one feature of a hair cosmetic polymer composition of the present invention resides in that the hair cosmetic polymer composition comprising (a) a block copolymer having a number-average molecular weight of 1.0×10^3 to 1.0×10^6 , and having two or more glass transition points or melting points and (b) an anionic polymer (b) in a ratio by weight ((a)/(b)) of 1/10 to 10/1.

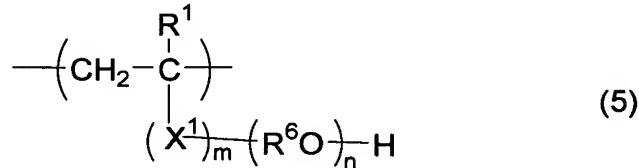
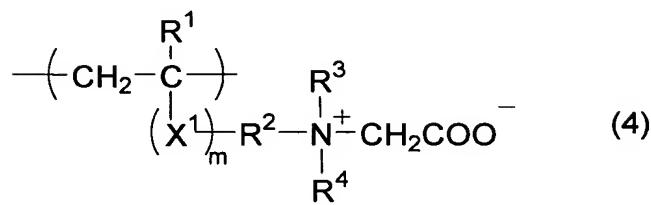
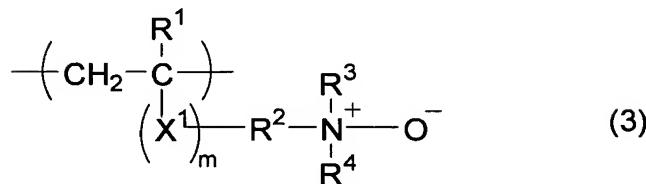
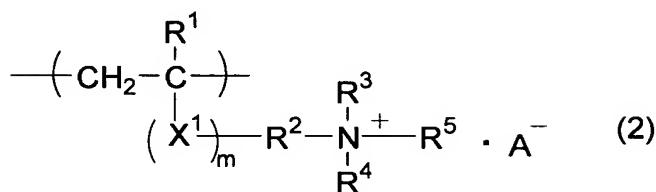
[0007]

As an embodiment of the present invention, the hair cosmetic polymer composition wherein the block copolymer (a) comprises at least one block formed of a unit having at least one hydrophilic group selected from groups consisting of an anionic group consisting of carboxylic acid group, sulfonic acid group, phosphonic acid group and salts of these groups; a cationic group consisting of amino group (including quaternary ammonium salt group), pyridyl group and salts of these groups; a nonionic group consisting of hydroxyl group, alkoxy group, epoxy group, amido group and cyano group; an amphoteric ionic group consisting of carboxybetaine group; and a semipolar group consisting of amine oxide group; the hair cosmetic polymer composition wherein the anionic polymer (b) is a polymer having an anionic group selected from carboxyl group, sulfonic acid group, phosphonic acid group and salts of these groups; or the hair cosmetic polymer composition wherein the block

copolymer (a) comprises at least one of units represented by formulae (1) to (5) below; is provided.

[0008]

[Chemical structure 2]



[0009]

In the formulae, R^1 represents a hydrogen atom or a methyl group; R^2 and R^6 respectively represent a C_{1-4} straight-chain or branched-chain alkylene group; R^3 , R^4 and R^5 respectively represent a hydrogen atom, C_{1-24} alkyl group, C_{6-24} aryl group, or any combination thereof such as C_{7-24}

arylalkyl group or alkylaryl group; and X¹ represents -COO-, -CONH-, -O- or NH-. A⁻ represents an anion; and M represents a hydrogen atom, an alkali metal ion or an ammonium ion. m is 0 or 1; and n is any integer from 1 to 50.

[0010]

And as an embodiment of the present invention, the hair cosmetic polymer composition wherein the block copolymer (a) is a di-block copolymer, tri-block copolymer or multi-block copolymer; the hair cosmetic polymer composition wherein the block copolymer (a) comprises a unit derived from an ethylenic unsaturated carboxylic acid in an amount of 10 to 90% by weight, and a unit derived from an ethylenic unsaturated carboxylate ester in an amount of 90 to 10% by weight; is provided.

[0011]

And, in another aspect, the present invention provides a hair cosmetic comprising the above mentioned hair cosmetic polymer composition in an amount of 0.1 to 10% by weight; and the hair cosmetic further comprising gas or liquid for spray.

[0012]

[Embodiments for carrying out the invention]

Next paragraphs will further detail the present invention. The hair cosmetic polymer composition of the present invention comprises (a) a block copolymer and (b) an anionic polymer.

The block copolymer (a) which can be used in the present invention has a number-average molecular weight of

1.0×10^3 to 1.0×10^6 , and has two or more glass transition points or melting points. The number-average molecular weight of the block copolymer is preferably from 1.0×10^3 to 1.0×10^6 . The number-average molecular weight less than 1.0×10^3 will result in a degraded film-forming ability. On the other hand, the number-average molecular weight of the block copolymer exceeding 1.0×10^6 may result in an increased viscosity of the solution extremely. When a hair cosmetic polymer composition is prepared, the polymers having the molecular weight falling within the above range can be used with other ingredients easily.

[0013]

The block copolymer of the present invention has two or more glass transition points or melting points. Of two glass transition points, the higher one is preferably 25°C or higher, more preferably 40°C or higher, and still more preferably 50°C or higher. Of two glass transition points, the lower one is preferably lower than 25°C , more preferably 0°C or lower, and still more preferably -20°C or lower. All of the melting points are preferably ambient temperature or around. The block copolymer preferably has a glass transition point or a melting point attributed to each block, and in other words, preferably has a glass transition point or a melting point nearly equal to the glass transition point or the melting point of a homopolymer composed of a monomer which makes up one block of the block copolymer. For example, a block copolymer of A-B type preferably has two glass transition points or melting points, where each of the glass transition points or melting

points is nearly equal to a glass transition point or a melting point individually attributed to homopolymers of A and B. On the other hand, a block copolymer of A-B-C type preferably has three glass transition points or melting points, where each of the glass transition points or melting points is nearly equal to a glass transition point or a melting point individually attributed to homopolymers of A, B and C.

It is noted that the term of "nearly equal to" is used not only for a situation of completely equal to each other and for a situation of permissibly equal to each other, but also for a situation of differing within 10 °C from each other.

[0014]

Although there is no specific limitation on the ratio (M_w/M_n) of weight-average molecular weight (M_w) to number-average molecular weight (M_n) of the block copolymer, measured by gel permeation chromatography, the ratio is preferably 2.5 or less, more preferably 2.0 or less, and still more preferably 1.8 or less. M_w/M_n exceeding 2.5 tends to degrade the uniformity of the block copolymer. The controlled radical polymerization process, described later, is successful in obtaining a uniform block copolymer having a small value of M_w/M_n .

[0015]

The block copolymer comprising at least one block having a hydrophilic group can readily be removed by hair wash, and is therefore preferably used for hair cosmetic material having an excellent hair washing property. The

block having a hydrophilic group is also advantageous in allowing the block copolymer to be blended with cosmetic materials in various forms. The hydrophilic group may be any of anionic group, cationic group, nonionic group and amphoteric group. Examples of the anionic group include carboxylic acid group, sulfonic acid group, phosphonic acid group and salts of these groups; examples of the cationic group include amino group (including quaternary ammonium group), pyridyl group and salts of these groups; examples of the nonionic group include hydroxyl group, alkoxy group, epoxy group, amido group and cyano group; examples of the amphoteric ionic group include carboxybetaine group, sulfobetaine group and phosphobetaine group; and examples of the semipolar group include amine oxide group. These hydrophilic groups can be introduced into the block copolymer by polymerizing a monomer originally having the hydrophilic group, or by subjecting the copolymer after being polymerized to a post-treatment such as hydrolysis.

It is to be noted that the semipolar group in the context of this patent specification does not mean an apparent ionic group, but instead means a group having both features of ionic bond and covalent bond, and having a biased electron distribution.

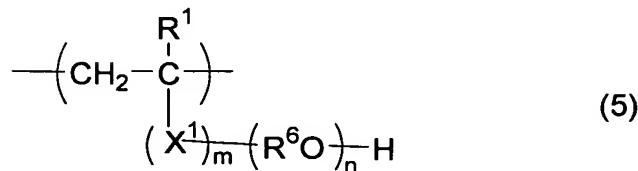
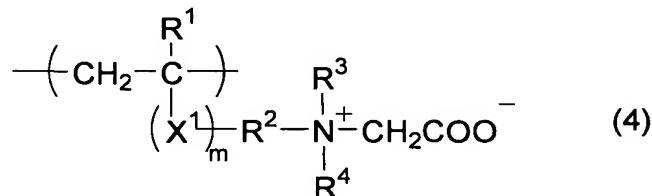
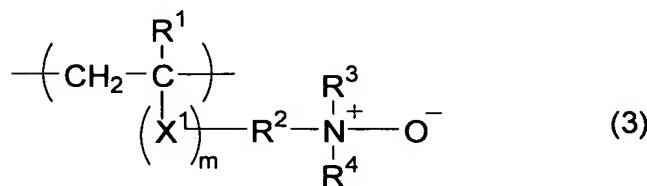
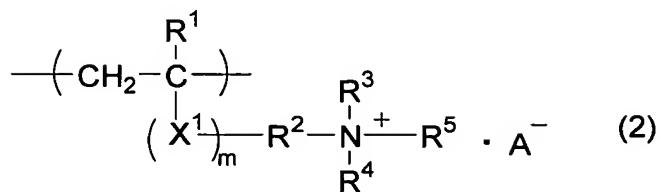
[0016]

As described above, the block copolymer preferably comprises at least one block formed of a unit having a hydrophilic group, and more preferably comprises at least one block formed of a unit derived from a compound having both of a hydrophilic group and an ethylenic unsaturated

bond. The unit having a hydrophilic group is preferably any one of units represented by the formulae (1) to (5) below.

[0017]

[Chemical structure 3]



[0018]

In the formulae, R¹ represents a hydrogen atom or a methyl group; R² and R⁶ respectively represent a C₁₋₄ straight-chain or branched alkylene group; R³, R⁴ and R⁵ respectively represent a hydrogen atom, a C₁₋₂₄ alkyl group, a C₆₋₂₄ aryl group, or any combination thereof such as C₇₋₂₄

arylalkyl group or alkylaryl group; and X^1 represents $-COO-$, $-CONH-$, $-O-$ or $NH-$. A^- represents an anion; and M represents a hydrogen atom, an alkali metal ion or an ammonium ion. m is 0 or 1; and n is any integer from 1 to 50.

[0019]

The C_{1-24} alkyl group respectively represented by R^3 , R^4 and R^5 include all of straight-chain, branched-chain and cyclic alkyl groups. The same will apply also to the alkyl group portion of the arylalkyl group and the alkyl group portion of alkylaryl group represented respectively by R^3 , R^4 and R^5 .

[0020]

Anion represented by A^- is exemplified by anionic group of acid, and specific examples thereof include halogen ion, sulfate ion and COO^- . Alkali metal ion represented by M can be exemplified by Na^+ and K^+ . Examples of ammonium ion represented by M not only include NH_4^+ derived from ammonia, but also include alkylammonium ions derived from amines such as volatile amines such as methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine, *n*-propylamine, *n*-butylamine, allylamine, ethylenediamine, morpholine and pyridine; and non-volatile amines such as mono-, di- or triethanolamine, mono-, di- or triisopropanolamine, aminoethyl propanol, aminoethyl propanediol and lysine.

[0021]

The block containing unit represented by any of the foregoing formulae (1) to (5) can be manufactured by using,

as a monomer, a double-bond-containing compound corresponded to any of the units represented by the formulae (1) to (5). Even for the case where the compounds corresponded to the units represented by the formulae (1) to (5) are not used, the block can be manufactured by polymerizing other monomer and subjecting the product to post-treatment such as hydrolysis. For example, a block copolymer having a block composed of the unit represented by the formula (1) can be manufactured also by using (meth)acrylic ester as a copolymerization monomer, in which a copolymer having a block composed of such monomer is synthesized, and the obtained block is then hydrolyzed. The block copolymer may be such as having two or more species of the blocks composed of the unit represented by any of the formulae (1) to (5).

[0022]

Examples of the compounds having ethylenic unsaturated bond, capable of composing the block copolymer, (including examples of the compounds capable of forming the units represented by the formulae (1) to (5)) are listed below, where the present invention is by no means limited by these specific examples.

Specific examples of the nonionic monomers include acrylic esters such as unsaturated methyl acrylate, ethyl acrylate, *n*-propyl acrylate, isopropyl acrylate, *n*-butyl acrylate, isobutyl acrylate, *t*-butyl acrylate, *n*-pentyl acrylate, *n*-hexyl acrylate, cyclohexyl acrylate, *n*-heptyl acrylate, *n*-octyl acrylate, 2-ethylhexyl acrylate, nonyl acrylate, decyl acrylate, dodecyl acrylate, phenyl acrylate, tolyl acrylate, benzyl acrylate, isobornyl

acrylate, 2-methoxyethyl acrylate, 3-methoxybutyl acrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, stearyl acrylate, glycidyl acrylate, 2-aminoethyl acrylate, γ -(methacryloyloxypropyl)trimethoxysilane, γ -(methacryloyloxypropyl)dimethoxysilane, ethylene oxide adduct of acrylic acid, trifluoromethylmethyl acrylate, 2-trifluoromethylethyl acrylate, 2-perfluoroethylacrylate, 2-perfluoroethyl-2-perfluorobutylethyl acrylate, 2-perfluoroethyl acrylate, perfluoromethyl acrylate, diperfluoromethyl methyl acrylate, 2-perfluoromethyl-2-perfluoroethyl methyl acrylate, 2-perfluorohexyl ethyl acrylate, 2-perfluorodecyl ethyl acrylate and 2-perfluorohexadecyl ethyl acrylate; aromatic alkenyl compounds such as styrene, α -methylstyrene, *p*-methylstyrene, and *p*-methoxystyrene; vinyl cyanide compounds such as acrylonitrile and methacrylonitrile;

[0023]

conjugated diene-base compounds such as butadiene and isoprene; halogen-containing unsaturated compounds such as vinyl chloride, vinylidene chloride, perfluoroethylene, perfluoropropylene and vinylidene fluoride; silicon-containing unsaturated compounds such as vinyl trimethoxysilane and vinyl triethoxysilane; unsaturated dicarboxylic acid compounds such as maleic anhydride, maleic acid, monoalkyl ester and dialkylester of maleic acid, fumaric acid, and monoalkyl ester and dialkyl ester of fumaric acid; vinyl ester compounds such as vinyl acetate, vinyl propionate, vinyl pivalate, vinyl benzoate and vinyl cinnamate; maleimide-base compounds such as maleimide,

methyl maleimide, ethyl maleimide, propyl maleimide, butyl maleimide, hexyl maleimide, octyl maleimide, dodecyl maleimide, stearyl maleimide, phenyl maleimide and cyclohexyl maleimide; methacrylic esters such as methyl methacrylate, ethyl methacrylate, *n*-propyl methacrylate, isopropyl methacrylate, *n*-butyl methacrylate, isobutyl methacrylate, *tert*-butyl methacrylate, *n*-pentyl methacrylate, *n*-hexyl methacrylate, cyclohexyl methacrylate, *n*-heptyl methacrylate, *n*-octyl methacrylate, 2-ethylhexyl methacrylate, nonyl methacrylate, decyl methacrylate, dodecyl methacrylate, phenyl methacrylate, tolyl methacrylate, benzyl methacrylate, isobornyl methacrylate, 2-methoxyethyl methacrylate, 3-methoxybutyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, stearyl methacrylate, glycidyl methacrylate, 2-aminoethyl methacrylate, γ -(methacryloyloxypropyl)trimethoxy silane, γ -(methacryloyloxypropyl)dimethoxy methyl silane, ethylene oxide adduct of methacrylic acid, trifluoromethyl methyl methacrylate, 2-trifluoromethyl ethyl methacrylate, 2-perfluoroethyl ethyl methacrylate, 2-perfluoroethyl-2-perfluorobutyl ethyl methacrylate, 2-perfluoroethyl methacrylate, perfluoromethyl methacrylate, diperfluoromethyl methyl methacrylate, 2-perfluoromethyl-2-perfluoroethyl methyl methacrylate, 2-perfluorohexyl ethyl methacrylate, 2-perfluorodecyl ethyl methacrylate, and 2-perfluorohexadecyl ethyl methacrylate;

[0024]

monomers derived from (meth)acrylate or (meth)acrylamide with C₂₋₄ alkylene oxide such as hydroxyethyl (meth)acrylate,

polyethylene glycol (meth)acrylate, methoxypoly(ethylene glycol/propylene glycol)mono(meth)acrylate, polyethylene glycol di(meth)acrylate and N-polyalkyleneoxy(meth)acrylamide; and hydrophilic nonionic monomers such as N-cyclohexyl maleimide, N-phenylmaleimide, N-vinylpyrrolidone, N-(meth)acryloyl morpholine and acrylamide.

It is noted that, in the *specification*, the term "(meth)acryl" or the like mean "acryl or methacryl".

[0025]

Specific examples of anionic monomer include unsaturated carboxylic acid compounds such as (meth)acrylic acid, maleic acid, maleic anhydride, itaconic acids, fumaric acid and crotonic acid; half ester compounds derived from an unsaturated polybasic acid anhydride (e.g., succinic anhydride, phthalic anhydride) and a hydroxyl-group-containing (meth)acrylate (e.g., hydroxyethyl (meth)acrylate); compounds having a sulfonic acid group such as styrenesulfonic acid and sulfoethyl (meth)acrylate; and compounds having a phosphonic acid group such as acid phosphooxyethyl(meth)acrylate. This anionic unsaturated monomer can be used in a form of intact acid or partially-neutralized or completely-neutralized form, or can be subjected to copolymerization in a form of intact acid and can partially or completely be neutralized. Examples of the base used for the neutralization include alkali metal hydroxide such as potassium hydroxide and sodium hydroxide; aqueous ammonia solution; and amine compounds such as mono-, di- and tri-ethanolamines, and trimethylamine.

[0026]

Specific examples of cationic monomer include cationic monomers obtained by cationizing N,N-dimethylaminoethyl (meth)acrylate, N,N-diethylaminoethyl (meth)acrylate, N,N-dimethylaminopropyl (meth)acrylate, N,N-diethylaminopropyl (meth)acrylate, N,N-dimethylaminoethyl (meth)acrylamide, N,N-diethylaminoethyl (meth)acrylamide, N,N-dimethylaminopropyl (meth)acrylamide, N,N-diethylaminopropyl (meth)acrylamide, p-dimethylaminomethyl styrene, p-dimethylaminoethyl styrene, p-diethylaminomethyl styrene or p-diethylaminoethylstyrene using a cationizing agent (e.g., alkyl halides such as methyl chloride, methyl bromide and methyl iodide; dialkyl sulfates such as dimethyl sulfate; epichlorohydrin-adduct of tertiary amine mineral acid salt such as N-(3-chloro-2-hydroxypropyl)-N,N,N-trimethylammonium chloride; inorganic acids such as hydrochloric acid, hydrobromic acid, sulfuric acid and phosphoric acid; and carboxylic acids such as formic acid, acetic acid and propionic acid).

[0027]

Specific examples of amphoteric monomer include compounds obtained by reacting the above-described examples of the cationic monomer precursors with a modifying agent such as sodium haloacetate or potassium. Specific examples of polarized monomer include amine oxides of N,N-dimethylaminoethyl (meth)acrylate, N,N-diethylaminoethyl (meth)acrylate, N,N-dimethylaminopropyl (meth)acrylate, N,N-diethylaminopropyl (meth)acrylate, N,N-dimethylaminoethyl (meth)acrylamide, N,N-diethylaminoethyl (meth)acrylamide,

N,N-dimethylaminopropyl (meth)acrylamide, N,N-diethylaminopropyl (meth)acrylamide, vinyl N,N-dimethylaminopropionate, *p*-dimethylaminomethylstyrene, *p*-dimethylaminoethylstyrene, *p*-diethylaminomethylstyrene and *p*-diethylaminoethylstyrene. These monomers can be used in a singular manner or in any combination of two or more species.

[0028]

Among these, acrylic esters, methacrylic esters, aromatic alkenyl compounds, vinyl cyanide compounds, conjugate diene-base compounds or halogen-containing unsaturated compounds are preferably used in view of its readiness in industrial availability.

[0029]

A preferable embodiment of the block copolymer can be exemplified by a block copolymer comprising at least one species each of a block composed of an ethylenic unsaturated carboxylic acid unit, and a block composed of an ethylenic unsaturated carboxylate ester unit. The ethylenic unsaturated carboxylic acid unit is preferably a unit which is derived from a hydrophilic monomer and has a high Tg. Preferred examples of such a unit include units derived from acrylic acid and methacrylic acid. On the other hand, the ethylenic unsaturated carboxylate ester unit is preferably a unit which is derived from a hydrophobic monomer and has a low Tg. Preferred examples of such a unit include units derived from acrylic esters and methacrylic esters. Compositional ratios of the ethylenic unsaturated carboxylic acid block and the ethylenic unsaturated carboxylate ester

block composing the polymer are preferably 10 to 90% by weight for the former, and 90 to 10% by weight for the latter, more preferably 15 to 80% by weight for the former, and 80 to 15% by weight for the latter, and still more preferably 20 to 50% by weight for the former and 80 to 50% by weight for the latter when more flexibility is desired. On the other hand, when some kind of rigidity is required, the ratio of the former is preferably 80 to 50 % and the ratio of the latter is preferably 20 to 50 %. The ethylenic unsaturated carboxylic acid block less than 10% by weight tends to make the block copolymer insoluble into water, and the ethylenic unsaturated carboxylate ester block less than 10% by weight tends to worsen the film-forming ability and to considerably degrade rubber elasticity of the polymer.

It is to be noted that "unit derived from a compound" in the context of this patent specification means not only a unit obtained after polymerizing the compound as a monomer, but also means a unit structurally derived from the compound obtained after the post-treatment such as hydrolysis as described in the above.

[0030]

The block copolymer may have any form of diblock copolymer, triblock copolymer and multi-block copolymer, without departing from the straight-chain structure. For example, the block copolymer having a hard block A (high-Tg block) and a soft block B (low-Tg block) may have any form of A-B diblock copolymer, A-B-A triblock copolymer, B-A-B triblock copolymer and $(A-B)_n$ multi-block copolymer. Among theses, A-B-A triblock copolymer, $(A-B)_n$ multi-block

copolymer and mixture of these are preferable in view of providing rubber elasticity to the polymer.

[0031]

The block copolymer may have a straight-chain structure or a branched-chain (star-shaped) structure, and may be selected from any mixtures thereof. The block copolymer having any structure may be used depending on the required properties.

[0032]

The block copolymer is preferably dispersible or soluble in water and/or alcohol. The solubility in water (or solubility in alcohol) of the block copolymer can be confirmed by stirring 1 weight part of the block copolymer and 99 parts by weight of deionized water and/or ethanol-mixed solution at 60°C for 2 hours, cooling the mixture, allowing the mixture to stand at room temperature for a day, and observing that the resultant aqueous solution is kept homogeneous without producing precipitate, and the resultant aqueous solution shows a light transmissivity of 70% or more at 655 nm. "Dispersible" in the context of this patent specification means that fine particles of the copolymer can disperse in water and/or alcohol without causing precipitation, and is kept in an emulsified form or latex form.

[0033]

Examples of the process for preparing the block copolymer (a) include, but are not limited to, processes employing ① to ④ methods shown below. Among these processes, processes employing ② living radical

polymerization, which is one of controlled radical polymerization, are preferred since molecular weights and structures of block copolymers to be prepared can be easily controlled.

- ① living anion or living cation polymerization
- ② living radical polymerization
- ③ suspension polymerization
- ④ method employing polymer initiator or chain transfer agent

[0034]

Living radical polymerization refers to a radical polymerization during which activity of the polymerization terminal is kept without being lost. Living polymerization in a narrow sense refers to polymerization during which the terminal keeps on maintaining the activity, but is generally understood as including also pseudo-living polymerization in which inactivated terminal and activated terminal are kept in an equilibrium. The latter meaning is adopted in this patent specification. In recent years, living radical polymerization has extensively been studied by many teams, and known achievements include a method using a chain-transfer agent such as polysulfide; methods using radical trapping agents such as cobalt porphyrin complex (J. Am. Chem. Soc., 1994, 116, 7943) and nitroxide compound (Macromolecules, 1994, 27, 7228); and atom-transfer radical polymerization (ATRP) using an organic halide as an initiator, and using a transition metal complex as a catalyst. Any of these methods may be adopted to the present invention, where atom-transfer radical

polymerization is preferably adopted in view of simplicity in the control.

[0035]

There is no specific limitation on the method of manufacturing the block copolymer, where the controlled radical polymerization based on the sequential addition of the monomers using copper halide as a catalyst together with amine ligand is preferable since such method is successful in facilitating control of the molecular weight of the resultant block copolymer.

[0036]

The block copolymer obtained by the polymerization may be used for the cosmetic polymer composition of the present invention in an intact form, or used after being subjected to the post-treatment such as hydrolysis. Control of the modification ratio by the post-treatment is successful in adjusting various characteristics of the resultant block copolymer, such as water solubility and film-forming ability, within a desirable range adaptive to the applications. Examples of the post-treatment include hydrolysis, quaternization and amine-oxide-forming treatment. An exemplary hydrolytic process can hydrolyze a block formed of acrylic ester, methacrylic ester or the like, to thereby produce an acrylic acid-derived or methacrylic acid-derived block having carboxylic acid group as a hydrophilic group (e.g., a block having the unit represented by the formula (1)). Hydrolysis of ester can be carried out by using an acid catalyst such as hydrochloric acid and *p*-toluenesulfonic acid, or a base catalyst such as

sodium hydroxide. The degree of hydrolysis can be controlled by the amount of use of the catalyst and reaction time. The carboxylic acid thus produced by the hydrolysis may be used after being partially or completely neutralized. A substance conveniently used for the neutralization is base, and examples of the base include alkali metal hydroxide such as potassium hydroxide and sodium hydroxide; and amine compounds such as aqueous ammonia solution, mono-, di- and tri-ethanolamines and trimethylamine.

[0037]

According to the present invention, an anionic polymer having an anionic group is used as the (b) ingredient with (a) ingredient, or, in other words, the block copolymer. As the anionic group, a carboxylic acid group, a sulfonic acid group, a phosphonic acid group and salts of these groups are preferred. Specific examples of the anionic polymer, which can be used as the (b) ingredient, include methyl vinyl ether/maleic anhydride alkyl half ester copolymer such as Gantrez ES-225, ES-425, A-425, V-225, V-425 (all of these are products of ISP); vinyl acetate/crotonic acid copolymer such as Resin 28-1310 (product of National Starch and Chemical Company) and Luviset CA (product of BASF AG); vinyl acetate/crotonic acid/vinyl neodecanoate copolymer such as Resin 28-2930 (product of National Starch and Chemical Company); vinyl acetate/crotonic acid/vinyl propionate copolymer such as Luviset CAP (product of BASF AG); vinyl acetate/monobutyl maleate/isobornyl acrylate copolymer such as Advantage CP (product of ISP); (meth)acrylic acid/(meth)acrylate copolymer such as Luvimer 100P (product

of BASF AG) and Diahold (product of Mitsubishi Chemical Corporation); acrylic acid/acrylamide derivative copolymer such as Ultrahold=Strong, Ultrahold 8 (two theses products are from BASF AG), Versatyle 42 (product of National Starch and Chemical Company) and Plascize L53P (product of Goo Chemical Co., Ltd.); poly(vinylpyrrolidone/(meth)acrylic acid/(meth)acrylate copolymer such as Luviflex VBM35 (product of BASF AG); diethylene glycol/cyclohexane dimethanol/dimethyl isophthalate/dimethyl sulfonated isophthalate condensate such as Eastman AQ Polymer (product of Eastman Chemical Company).

[0038]

The anionic group in the anionic polymer (b) is preferably used in a form of partially or completely neutralized with a basic compound, in view of water solubility. Examples of such basic compound include alkali metal hydroxide such as sodium hydroxide and potassium hydroxide; inorganic basic compounds such as aqueous ammonia; alkanol amines such as ethanolamine, diethanolamine, triethanolamine, triisopropanolamine, 2-amino-2-methyl-1-propanol, 2-amino-2-methyl-1,3-propanediol, aminomercaptopropanediol; basic amino acids such as lysine, arginine and histidine. Among these, 2-amino-2-methyl-1-propanol and potassium hydroxide are particularly preferable in view of water solubility.

[0039]

The anionic polymer (b) preferably contain the anionic group in an amount of 5% by weight or more, more preferably 10% by weight or more, and still more preferably 15% by

weight or more.

[0040]

Weight-average molecular weight of the anionic polymer (b) preferably falls within a range from 5,000 to 1,000,000, more preferably from 10,000 to 500,000, and still more preferably from 20,000 to 300,000.

[0041]

In one embodiment relating to the hair cosmetic polymer composition, ratio by weight ((a)/(b)) of the block copolymer (a) to anionic polymer (b) preferably falls in a range from 1/10 to 10/1, and more preferably from 1/5 to 10/1. The ratio (a)/(b) less than 1/10 may result in a poor flexibility, a stiff touch on the hair, a poor styling ability, and difficulty in setting hair due to flaking or static electricity during combing hairs. On the other hand, the ratio exceeding 10/1 may result in a poor elasticity and volume in the hair styling due to insufficient hardness, a heavy finish, and a degraded feel of touch in the finished style. The hair cosmetic polymer composition of the present invention preferably contains the component (a) and component (b) in an amount of 0.1 to 10% by weight of the total composition, and more preferably 0.5 to 8% by weight. A content of less than 0.1% by weight tends to result in a poor hair styling ability, and of exceeding 10% by weight may add a stiff touch and worsen the feel of touch.

[0042]

The hair cosmetic polymer composition of the present invention may comprise other general ingredient of cosmetics, besides the foregoing (a) and (b) ingredients,

within a range not affective to the effects of the present invention. Examples of the other general ingredient include glycerides such as caster oil, cacao seed oil, mink oil, avocado oil, jojoba oil, macadamia nuts oil and olive oil; waxes such as yellow bees wax and lanolin; hydrocarbons such as liquid paraffin, solid paraffin, isoparaffin and squalane; straight-chain and branched-chain higher alcohols such as cetyl alcohol, oleyl alcohol, stearyl alcohol, isostearyl alcohol, lauryl alcohol and 2-octyl dodecanol; polyalcohols such as ethylene glycol, polyethylene glycol, propylene glycol, polypropylene glycol, glycerin and sorbitol; ethylene oxide and/or propylene oxide adducts of higher alcohol such as polyoxyethylene lauryl ether, polyoxypropylene cetyl ether and polyoxyethylene polyoxypropylene stearyl ether; esters such as isopropyl myristate, octyl dodecyl myristate, hexyl laurate and cetyl lactate; amides such as oleic acid diethanolamide and lauric acid diethanolamide; silicone derivatives such as dimethylpolysioxane, methylphenylpolysiloxane, polyether degeneration silicone and amino degeneration silicone; cationic surfactants such as stearyl trimethyl ammonium chloride, distearyl dimethyl ammonium chloride and lauryl trimethyl ammonium chloride; anionic surfactants such as polyoxyethylene lauryl ether sulfate, polyoxyethylene lauryl sulfo succinate; amphoteric surfactants such as lauryl hydroxy sulfobetaine and lauryldimethyl carboxybetaine; protein derivatives or amino acid derivatives such as collagen hydrolysate, keratin hydrolysate and polyamino acids; plant extracts, crude drugs, vitamins, ultraviolet

absorbers such as oxybenzene, chelating agents such as EDTA-Na, preservatives such as paraben, antioxidants, dyes, pigments and flavoring ingredients.

[0043]

The hair cosmetic of the present invention is characterized by comprising the hair cosmetic polymer composition comprising the (a) ingredient and the (b) ingredient. In the hair cosmetic of the present invention, the content of the composition is preferably from 0.1 to 10 % by weight and more preferably from 0.5 to 8 % by weight with respect to the total weight of the hair cosmetic. A content of less than 0.1% by weight tends to result in a poor hair styling ability, and of exceeding 10% by weight may add a stiff touch and worsen the feel of touch. It is noted that when the composition comprising other general ingredients, the total weight of the (a) ingredients and the (b) ingredients in the hair cosmetic is preferably from 0.1 to 10 % by weight and more preferably from 0.5 to 8 % by weight.

[0044]

The applications or the modes of the hair cosmetic of the present invention is not to be limited to, and the hair cosmetic of the present invention may be used as any types of aerosol hair spray, pump-type hair spray, foam-type hair spray, hair mist, styling lotion, hair gel, hair cream and hair oil. The hair cosmetic of the present invention can be prepared by dissolving and/or dispersing ingredients, including the (a) ingredient and the (b) ingredient, in a solvent such as water and/or alcohols such as ethanol and

isopropanol. And chlorfluoro alkanes such as trichloro-monofluoro methane and dichloro-difluoro methane; liquefied petroleum gases formed of alkanes; dimethylether; compressed gases such as carbon dioxide gas and nitrogen gas; and mixed gases thereof; may be used as spray gases or liquids according to common procedures, thereby to form aerosol type materials.

[0045]

[Examples]

The following paragraphs will specifically describe the present invention referring to exemplary manufacture and embodiments, where it is to be understood that the present invention is by no means limited to these exemplary manufacture and embodiments.

[Example 1] (Exemplary Manufacture of 2-Ethylhexyl Acrylate/*t*-Butyl Acrylate-Base Block Copolymer)

In a nitrogen-replaced reaction vessel equipped with a thermocouple and a stirring propeller, 165 mg of copper (I) bromide was placed and then heated to 80°C. The content of the reaction vessel, under the nitrogen atmosphere and stirring at 250 rpm, was further added with a mixed solution containing 692 mg of dimethyl-2,6-dibromoheptane dioate, 184 g of 2-ethylhexyl acrylate, 398 mg of pentamethyldiethylene triamine and 88 g of dimethylformamide. After stirred for 3 hours, the reaction vessel was quickly cooled in an ice bath to thereby terminate the reaction. The reaction solution was added with a mixed solution of tetrahydrofuran and water to separate into a layer containing polymer and a layer containing catalyst, and, after the copper bromide was

removed, the layer containing polymer was added dropwise to a large amount of methanol to allow the polymer to re-precipitate, and the solvent was removed by filtration. It was found that the inversion rate of 2-ethylhexyl acrylate was 50 %. The resultant polymer (occasionally referred to as "poly 2-ethylhexylacrylate macro-initiator", hereinafter) was found to have a weight-average molecular weight (M_w) of 33,000, number-average molecular weight (M_n) of 24,000, and molecular weight distribution (M_w/M_n) of 1.38.

[0046]

In a nitrogen-replaced reaction vessel equipped with a thermocouple and a stirring propeller, 28.6 mg of copper (I) bromide and 9.33 mg of copper (II) bromide was placed and then heated to 80°C. The content of the reaction vessel, under the nitrogen atmosphere and stirring at 250 rpm, was further added with a mixed solution containing 48 g of poly 2-ethylhexyl acrylate macro-initiator, 128 g of *t*-butyl acrylate, 79.7 mg of pentamethyl diethylene triamine, and 53 g of dimethylformamide. After stirred for 2 hours, the reaction vessel was quickly cooled in an ice bath to thereby terminate the reaction. The reaction solution was added with a mixed solution of tetrahydrofuran and water to separate into a layer containing polymer and a layer containing catalyst, and the layer containing polymer was allowed to pass through an aluminum silicate column (Kyoward 700SN, product of Kyowa Chemical Industry Co., Ltd.) to thereby completely remove copper bromides, the eluate was dropped into a large amount of methanol to thereby allow the polymer to re-precipitate, and the solvent

was removed by filtration. The resultant polymer was found to have a weight-average molecular weight (M_w) of 56,000, number-average molecular weight (M_n) of 39,800, and molecular weight distribution (M_w/M_n) of 1.41.

Weight fractions of 2-ethylhexyl acrylate and *t*-butyl acrylate in the block copolymer calculated from M_n were found to be 60% by weight and 40% by weight, respectively. The weight fractions of 2-ethylhexyl acrylate and *t*-butyl acrylate in the block copolymer were also confirmed by ^1H -NMR. The obtained block copolymer was a triblock copolymer having a formulation of poly(*t*-BA)/poly(2EHA)/poly(*t*-BA).

[0047]

Twenty one grams of thus obtained triblock copolymer of 2-ethylhexyl acrylate and *t*-butyl acrylate was dissolved into 480 ml of 1,4-dioxane. The mixture was then added with 33 mL of 6 mol/L hydrochloric acid, and refluxed under heating in an oil bath at 120°C for 6 hours. The mixture was then cooled, the solvent was condensed under reduced pressure, the residue was re-precipitated in a large amount of hexane, and the solvent was removed by filtration. The obtained polymer was washed with a large amount of water, and dried under reduced pressure to thereby obtain block copolymer P-1.

Ratio of hydrolysis of thus obtained block copolymer P-1 was confirmed by acid value titration using a 0.1 mol/L aqueous potassium hydroxide solution, and was found to be 61%. Glass transition temperature (T_g) was found to be -50°C for the 2-ethylhexyl acrylate block, 43°C for the *t*-butyl acrylate block and 107°C for the acrylic acid block.

These glass transition temperatures were found to be nearly equal to those of the homopolymers of the monomers respectively.

[0048]

[Exemplary Manufacture 2] (Exemplary Manufacture of 2-Ethylhexyl Acrylate/*t*-Butyl Acrylate-Base Block Copolymer P-2)

A poly 2-ethylhexyl acrylate macro-initiator was produced in the same manner as Example 1, except that the stirring was proceeded for 2 hour using 173 mg of copper (I) bromide, 697 mg of dimethyl-2,6-dibromoheptane dioate, 184 g of 2-ethylhexyl acrylate and 419 mg of pentamethyl diethylene triamine. It was found that the inversion rate of 2-ethylhexyl acrylate was 50 %. The obtained polymer was found to have a weight-average molecular weight (M_w) of 23,300, number-average molecular weight (M_n) of 16,400, and a molecular weight distribution (M_w/M_n) of 1.41.

[0049]

In a nitrogen-replaced reaction vessel equipped with a thermocouple and a stirring propeller, 717 mg of copper (I) bromide and 58.3 mg of copper (II) bromide was placed and then heated to 80°C. The content of the reaction vessel, under the nitrogen atmosphere and stirring at 250 rpm, was further added with a mixed solution containing 30 g of poly 2-ethylhexyl acrylate macro-initiator, 151 g of *t*-butyl acrylate, 1g of pentamethyl diethylene triamine, and 66 g of dimethylformamide. After stirred for 3 hours, the reaction vessel was quickly cooled in an ice bath to thereby terminate the reaction. After that, the reaction solution

was treated in the same manner as Example 1, and, thus, a copolymer was obtained. The resultant polymer was found to have a weight-average molecular weight (M_w) of 45,000, number-average molecular weight (M_n) of 25,400, and molecular weight distribution (M_w/M_n) of 1.77. Weight fractions of 2-ethylhexyl acrylate and *t*-butyl acrylate in the block copolymer calculated from M_n were found to be 47% by weight and 53% by weight, respectively. The weight fractions of 2-ethylhexyl acrylate and *t*-butyl acrylate in the block copolymer were also confirmed by $^1\text{H-NMR}$. The obtained block copolymer was a triblock copolymer.

[0050]

Eighteen grams of thus obtained triblock copolymer of 2-ethylhexyl acrylate and *t*-butyl acrylate was dissolved into 500 ml of 1,4-dioxane. The mixture was then added with 36 mL of 6 mol/L hydrochloric acid, and refluxed under heating in an oil bath at 120°C for 20 hours. The mixture was then cooled, the solvent was condensed under reduced pressure, the residue was re-precipitated in a large amount of hexane, and the solvent was removed by filtration. The obtained polymer was washed with a large amount of water, and dried under reduced pressure to thereby obtain block copolymer P-2.

Ratio of hydrolysis of thus obtained block copolymer P-2 was confirmed by acid value titration using a 0.1 mol/L aqueous potassium hydroxide solution, and was found to be 50%. Glass transition temperature (T_g) was found to be -50°C for the 2-ethylhexyl acrylate block, 43°C for the *t*-butyl acrylate block and 107°C for the acrylic acid block.

These glass transition temperatures were found to be nearly equal to those of the homopolymers of the monomers respectively.

[0051]

The molecular weights and molecular weight distributions were measured by GPC through a polystyrene gel column using tetrahydrofuran as a mobile phase, and determined on polystyrene basis.

The glass transition temperatures were measured by DSC (differential scanning calorimetry) at a temperature elevation speed of 20°C/min conforming to JIS K7121. In the following examples, they were measured in the same manner.

[0052]

[Example 3] (Manufacture of Random Copolymer having an amine oxide group)

In a reaction vessel attached with a reflux condenser, a dropping funnel, a thermometer, a nitrogen-replacement glass tube and a stirrer, 50 parts of N,N-dimethylaminoethyl methacrylate, 30 parts of methyl methacrylate, 20 parts of isobutyl methacrylate, and 150 parts of dehydrated ethanol were placed, 0.6 part of 2,2'-azobis(isobutyronitrile) was added, and the mixture was refluxed at 80°C under nitrogen-replaced atmosphere for 8 hours so as to proceed reaction and cooled by 60 °C.

[0053]

The polymerization solution was added dropwise with 31 % aqueous solution of hydrogen peroxide in a molar amount equal to a molar mount of N,N-dimethylaminoethyl methacrylate with a dropping funnel for an hour, stirred for

20 hours to proceed oxidation of dimethyl amino groups, and added with a dehydrated ethanol to give a reaction solution of polymer with a concentration of 30 %. The termination of the oxidation reaction was confirmed by measurement of amine number of the obtained reaction solution. The obtained polymer was named "P-3". The weight-average molecular weight of the obtained polymer was found to be 110,000. The IR spectrum showed a N-O band indicating that amine oxide group was generated.

[0054]

[Example Nos. 1 to 3, Comparative Example Nos. 1 to 6]

Hair cosmetic materials having formulations shown in Table 1 were prepared by general procedures, applied to the hair, and evaluated for their hair styling performance (curl-retention performance), elasticity and stiffness of the hair, flaking, antistatic measures (surface resistance) after being coated on a polypropylene film, styling power (bending strength of hair yarn bundle) and style-keeping performance (strength of hair yarn bundle after fracture) according to the following procedures. As is obvious from the results shown in Table 1, the hair cosmetic materials of Example Nos. 1 to 3 had an excellent hair styling performance, successfully kept the curled shape of the hair even under a high-temperature-high-humidity environment, gave elasticity and volume in the hair style, showed no flaking, showed an excellent antistatic property, and had a desirable style-keeping performance by virtue of its elasticity. On the contrary, the hair cosmetic materials of Comparative Example Nos. 1 to 6 resulted in only an

insufficient styling performance, failed in providing volume in the hair style, caused flaking, and gave an insufficient antistatic property, all of which were undesirable in terms of performance.

[0055]

<Methods of Testing and Evaluation>

(1) Styling Performance (Curl-Retention Performance)

A straight hair yarn bundle of 23 cm in length and 2 g in weight was applied with the hair cosmetic material through a dispenser (or sprayed in a form of aerosol), immediately wound around 1.2-cm diameter curling rod, and dried. The hair yarn bundle removed from the curling rod was hung in a thermo-hygrostat chamber conditioned at 30°C, 95% RH, elongation of the hair yarn bundle was measured, and the obtained value was placed in the equation for evaluating curl retention below to thereby determine curl-retention performance (%).

Equation for evaluationg curl retention:

Curl-retention performance (%) = $[(23-L)/(23-L_0)] \times 100$
(where, L_0 is length (cm) of the hair yarn bundle immdiatey after being removed from the curling rod, and L is length (cm) of the curled hair 3 hours after).

○ : Curl-retention performance of 71% or more.

△ : Curl-retention performance of 40% or more and less than 70%.

× : Curl-retention performance of less than 40%.

[0056]

(2) Elasticity and stiffness of Hair Yarn

The hair yarn bundle was processed similarly to as

described in the style-keeping performance (curl-retention performance) test described in the above, the resultant curled hair yarn bundle was allowed to stand under a thermo-hygrostatic condition of 23°C, 60% RH, and elasticity of the hair yarn when crushed between fingers was evaluated.

○ : Enough stiffness and desirable elasticity.

△ : Enough stiffness but poor elasticity and brittle.

× : No elasticity and not good touch.

[0057]

(3) Flaking

A straight hair yarn bundle of 23 cm in length and 2 g in weight was applied with the hair cosmetic material through a dispenser (or sprayed in a form of aerosol), immediately flattened with fingers to thereby prepare a flat plate-formed hair yarn bundle, and dried. The hair yarn bundle was then allowed to stand under a condition of 23°C, 60% RH, combed, and the amount of dropped polymer flakes remaining on the hair yarns was observed under a stereomicroscope (×20).

○ : No polymer flake observed, or only slightly observed.

△ : Polymer flake observed.

× : A large amount of polymer flake observed.

[0058]

(4) Antistatic Property (Surface Resistivity)

Liquid of the hair cosmetic material listed in Table 1 was prepared (liquid of the hair cosmetic material intended for use in combination with an injection agent (dimethyl ether: DME, liquefied petroleum gas :LPG) is prepared by adding ethanol in the same weight with the injection agent,

before being filled into a spray can). The obtained solution was coated on a discharge-treated polypropylene film using a 22-mil bar coater, dried using a hair dryer, allowed to stand under a condition of 23°C, 60% RH, and the surface resistivity was measured using an insulation resistance meter (High Megohm Meter: product of Takeda Riken Kogyo K.K.)

- : Surface resistance of less than 1×10^{10}
- △ : Surface resistance of 1×10^{10} or above but less than 1×10^{12}
- × : Surface resistance of 1×10^{12} or above.

[0059]

(5) Styling Ability Test (Bending Strength of Hair Yarn Bundle)

A hair yarn bundle of 15 cm long was applied with 0.7 g of the individual samples, immediately shaped in 2-cm width, dried, and allowed to stand for one hour in a thermo-hygrostat chamber conditioned at 23°C, 60% RH. The sample was then placed on the supports 65 mm distant from each other and bent at the center thereof under a constant speed, and maximum load was measured and evaluated according to the following criteria.

- : The maximum load was 200 g or above, and the coated hairs were soft to the touch and there was no incompatibility after measurement.
- △ : The maximum load was 100 g or more, and the coated hairs were soft to the touch, but there was a certain level of incompatibility after measurement.
- × : The maximum load was less than 100 g, and the coated

hairs were not soft to the touch, and there was incompatibility after measurement.

[0060]

(6) Style-Keeping Ability Test (Hair Yarn Bundle Bending Test)

After the style-keeping performance test, maximum load after the hair yarn bundle was broken was evaluated according to the following criteria.

○ : Maximum load was 15 g or more.

△ : Maximum load was 10 g or more and less than 15 g.

× : Maximum load was less than 10 g.

[0061]

[Example Nos. 4 to 7, Comparative Example Nos. 7 to 10]

Hair cosmetic materials (water-containing aerosol or water-not-containing aerosol) having a formulation shown in Table 2 were prepared by general procedures, and evaluated similarly to as described for Example No. 1. As is obvious from the results shown in Table 2, the hair cosmetic materials of Example Nos. 4 to 7 had an excellent hair styling performance, successfully kept the curled shape of the hair even under a high-temperature-high-humidity environment, gave elasticity and volume in the hair style, showed no flaking, showed an excellent antistatic property, and had a desirable style-keeping performance by virtue of rubber elasticity of the polymer film. On the contrary, the hair cosmetic materials of Comparative Example Nos. 7 to 10 resulted in only an insufficient styling performance, failed in providing volume in the hair style, caused flaking, and gave an insufficient antistatic property, all of which were

undesirable in terms of performance.

[0062]

[Table 1]

		Example			(%:Conversion amounts of activate ingredients)					
		1	2	3	1	2	3	4	5	6
Composition	P-2	2.0	2.0	2.0	—	—	—	—	—	—
	Anionic polymer 1	1.0	—	—	3.0	—	—	1.0	—	—
	Anionic Polymer 2	—	1.0	—	—	3.0	—	—	1.0	—
	Anionic Polymer 3	—	—	1.0	—	—	3.0	—	—	1.0
	P-3	—	—	—	—	—	—	2.0	2.0	2.0
	Pure water	45.0	45.0	45.0	45.0	45.0	45.0	45.0	45.0	45.0
Evaluation results	Ethanol	balance	balance	balance	balance	balance	balance	balance	balance	balance
	Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
	(1) Styling ability	○	○	○	△	×	×	○	○	○
Evaluation results	(2)Elasticity and volume of hairs	○	○	○	△	△	△	○	○	○
	(3)Flaking	○	○	○	×	×	×	○	○	○
	(4)Antistatic Property	○	○	○	×	×	×	○	○	○
	(5)Styling Performance	○	○	○	○	○	○	△	△	△
	(6)Style-Keeping ability	○	○	○	×	×	×	△	×	×

[0063]

[Table 2]

		Example									
		4	5	6	7	8	9	10			
Composition	P-1	2.0	2.0	—	—	—	—	—	—	—	—
	P-2	1.0	—	2.0	2.0	—	—	—	—	—	—
	Anionic polymer 1	—	1.0	—	—	3.0	—	1.0	—	—	—
	Anionic Polymer 2	—	—	1.0	—	—	3.0	—	—	1.0	—
	P-3	—	—	—	1.0	—	—	2.0	2.0	2.0	2.0
	Pure water	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0
Evaluation results	Ethanol	balance									
	Concentrate solution	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0
	LPG	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
	DME	30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0
Evaluation results	Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
	(1) Styling ability	○	○	○	○	×	×	○	○	○	○
	(2)Elasticity and volume of hairs	○	○	○	○	△	△	○	○	○	○
	(3)Flaking	○	○	○	○	×	×	○	○	○	○
	(4)Antistatic Property	○	○	○	○	×	×	○	○	○	○
	(5)Styling Performance	○	○	○	○	○	○	△	△	△	△
Evaluation results	(6)Style-Keeping ability	○	○	○	○	×	×	△	△	△	×

[0064]

P-1: Block copolymer prepared in Exemplary Manufacture 1

P-2: Block copolymer prepared in Exemplary Manufacture 2

P-3: Amine-oxide-group-containing copolymer prepared in

Exemplary Manufacture 3

Anionic polymer 1: Diahold LP503 (product of Mitsubishi Chemical Corporation)

Anionic polymer 2: Partially nuetrized product obtained by neutralizing 20 mol% of acid portion of Gantrez ES-225 (product of ISP) with 2-amino-2-methyl-1-propanol

Anionic polymer 3: Partially nuetrized product obtained by neutralizing 90 mol% of acid portion of Resin 28-2930 (product of National Starch and Chemical Company) with 2-amino-2-methyl-1-propanol.

[0065]

[Effect of the invention]

As described above, according to the present invention, it is possible to solve the problems of conventional hair cosmetic polymer compositions employing anionic polymers, and to provide a cosmetic polymer composition and a hair cosmetic material (various types of hair cosmetic material such as a hair spray, a hair muse, a hair set lotion, a hair gel or the like) having an excellent hair-styling ability and a good hair-style-keeping ability due to the elasticity and giving natural-feeling finishing without unpleasant feeling.

[Name of document] Abstract

[Abstract]

[Object] To provide a hair cosmetic polymer composition having an excellent hair-styling ability and a good hair-style-keeping ability and giving natural-feeling finishing without unpleasant feeling.

[Means for solving the problems] A hair cosmetic polymer composition comprising (a) a block copolymer having a number-average molecular weight of 1.0×10^3 to 1.0×10^6 , and having two or more glass transition points or melting points and (b) an anionic polymer (b) in a ratio by weight ((a)/(b)) of 1/10 to 10/1 is provided.

[Representative drawing] None